interpretation, it is interesting to note that the demarcation between the old, high marsh and the lower, more recent marsh (less than 100 years old) is frequently made clearly visible elsewhere in the aerial photographs by the deposition of drift logs at the declivity between the two types of marsh and by the drier nature of the high marsh.

Similar circular colonies of marsh plants are found on expanding marshes in the Tillamook, Umpqua, Coos, and Coquille estuaries. Only in the Alsea estuary, of those investigated, has there been practically no marsh expansion during the last 100 years; with one small exception, no circular colonies exist along the margin of the marsh. This exception is in front of a levee, built in 1958, that effectively blocks a slough and changes the tidal flow in the main channel of the river. Because of the levee, sediments have been deposited recently and marsh plants, especially sea arrow grass, have colonized rapidly.

In summary, the appearance of abundant circular clumps of vegetation, 0.3 to 15 meters in diameter, in aerial photographs of estuarine mud flats in temperate regions predicts that the marshes are expanding rapidly.

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4. Supported by contract ONR 2771 (04), project NR 388-062, and by the Graduate School, University of Oregon.

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Ancient Copper and Copper-Arsenic Alloy Artifacts: Composition and Metallurgical Implications

Abstract. *Various copper and copper-arsenic alloy artifacts from the Dead Sea area lack the tin and zinc that are normal trace elements. The trace elements found in the artifacts suggest that a copper sulf-arsenate ore was used in making some of them. The metallurgical use of such ore around 3000 B.C. has not been previously reported.*

Unlike our knowledge of early pottery, little is known of the development of metallurgical techniques. Very few early metal artifacts are found sufficiently well preserved. Analyses have been difficult, and systematic analyses of trace elements are not found in the archeological literature on finds made in the Middle East, although much work has been done on artifacts from western Europe. In the Middle East the archeologist has usually been interested only in tin content to determine whether or not he is dealing with bronze artifacts.

It has been assumed that the art of metallurgy developed over a fairly long period and that considerable time elapsed between the first use of copper, smelted from green, easily recognized copper ore [as in Egypt (*1*)] and the later use of copper sulfide ores which needed the double process of roasting and smelting (*2*).

The discovery of a large hoard of excellently preserved copper and copper-alloy objects enables us to reconsider these views. The hoard was found buried, wrapped up in a thin reed mat, in a cave in the extremely arid Dead Sea region. The find is described, with archeological details, in another paper (*3*). Carbon-14 determinations on the mat gave an age of approximately 5000 years. Such a minimum age for the metal objects agrees well with the archeological similarities to other late-Chalcolithic finds.

The metal objects of this unique hoard comprised 240 "mace-heads," 80 "staff-heads" or "wands," 10 crowns, and 20 chisels or axes; they were covered by black organic grime but had no oxide coating (Figs. 1 and 2). Preliminary x-ray fluorescence examination by L. Heller of the Geological Survey of Israel revealed significant amounts of arsenic in some of the mace-heads, amounts that led me to believe that sulfide ores had been the source of the copper. Eleven mace-heads, 11 staff-heads, and 8 tools were investigated, as well as a similar staff-head, badly oxidized, from Beersheba and a mace-head and a chisel found in a cave in Wadi Nahal Tse'elim nearby.

Emission spectrographic methods were then used to determine As, Sb, Ag, Bi, Pb, and Ni, which were present as traces or in greater amounts. Tin and zinc were sought but not found in any of the objects analyzed. The equipment consisted of a quartz-glass spectrograph and a high-voltage condensed spark unit. The very well-preserved objects were rubbed lightly with sand-paper before sparking. A National spectrographic graphite upper electrode was used, and the sample was excited at 0.03 mh and 15 kv, with a 10-second prespark followed by a 60-second exposure; the gap was 2 mm. The spectra were photographed on Kodak 103-0 plates and developed normally. The relative deviation from the mean of duplicate determinations on four standard samples was 12 percent for Pb and less than 10 percent for the other elements determined. Replicate determinations to detect possible variations at the surfaces of three objects and on a freshly sawn face in one object also fell within these limits.

Results of some of the spectrographic analyses are presented in Table 1. The 22 ornaments all contain silver; only one lacks nickel, two lack antimony, three lack bismuth, and five lack measurable amounts of arsenic. This indicates that the ornaments either are the products of one workshop or reflect the use of one rough formula. With one exception, the tools, by contrast, are of impure but unalloyed copper.

Table 1. Minor elements of five artifacts (percentages).

Specimen No.	As	Sb	Ag	Bi	Pb	Ni
			Ornaments			
351	3.50	0.178	0.123	0.0013	0.034	0.170
121	11.90	0.609	0.210	0.0240	0.039	1.22
(Beersheba)	12.00	0.715	0.258	0.0420	Trace	0.048
			Tools			
147	1.92	Trace	.010			
148			.042			1.90

Scatter diagrams (Fig. 3) for the ornaments show that antimony and silver contents are directly proportional to the arsenic contents. The range in bismuth values is from 10 parts per million to 250 ppm; bismuth content is proportional to the amount of silver, and hence proportional to arsenic. Nickel content ranges from 0.1 to 3 percent and lead from 0.03 to 2.40 percent; neither element relates to the arsenic content.

Arsenic, antimony, silver, and bismuth are associated with copper only in a sulf-arsenate ore such as enargite and tenantite; not in green copper-carbonate ores. The nickel content indicates the use of a copper-sulfide ore, either alone (as for the tools) or perhaps as an admixture for the alloy. The lead content is not easily explained but, since several specimens have had casting defects repaired with lead, it may be that lead is only an accidental admixture.

The absence of zinc and tin from all objects is surprising and highly significant when the source of the ore is considered. I analyzed copper ores from southern Israel and Cyprus and artifacts from Loristan and Amlash in the Zagros Mountains. All these materials contained either zinc or tin, or both; they are all known to derive from deposits exploited by the ancients. The earliest copper artifacts of Mesopotamia also contain traces of tin (*4*).

The difference in composition between the ornaments and tools shows up in the finished article. All articles made of alloyed copper are finished off to very close tolerances so that they are almost perfectly rounded. This is also the case with the one axe, which is well polished. The artisans attempted to make a staff-head, although an ornament, in unalloyed copper; it shows casting defects, the usual bottom flange is missing, and it has been left unpolished. The tools of unalloyed copper, on the other hand, are all very simple shapes and left rough; this may be either because they are older than the ornaments or because they were made by different craftsmen.

Fig. 1. Copper staff-head from the Dead Sea region; about 3000 B.C. Scale, 2 cm. [Photograph, Braun and Harris]

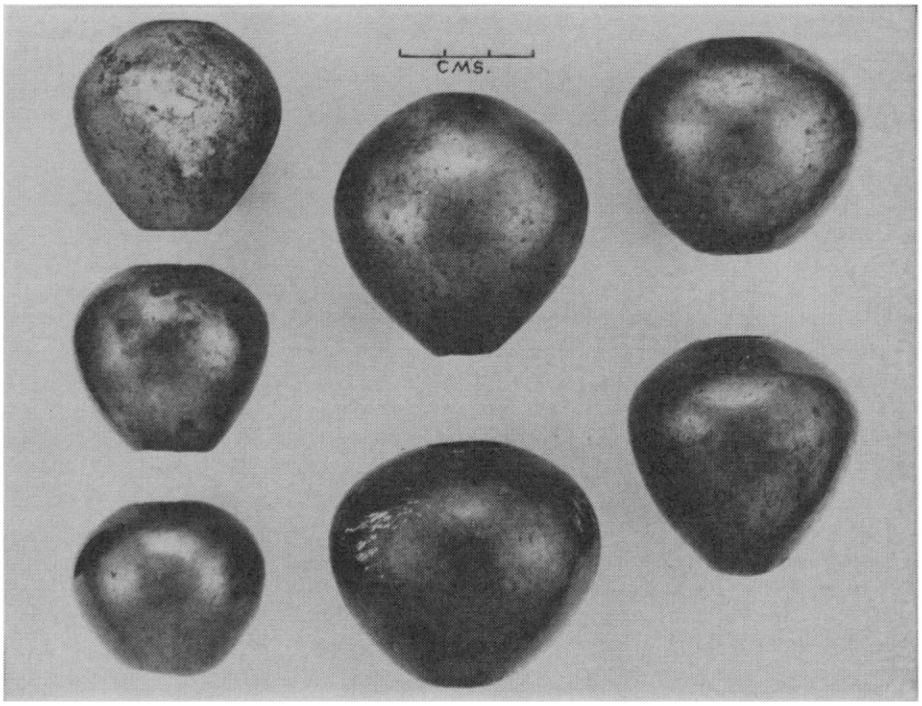

Fig. 2. Copper mace-heads from the Dead Sea region; about 3000 B.C. [Photograph, J. Schweig]

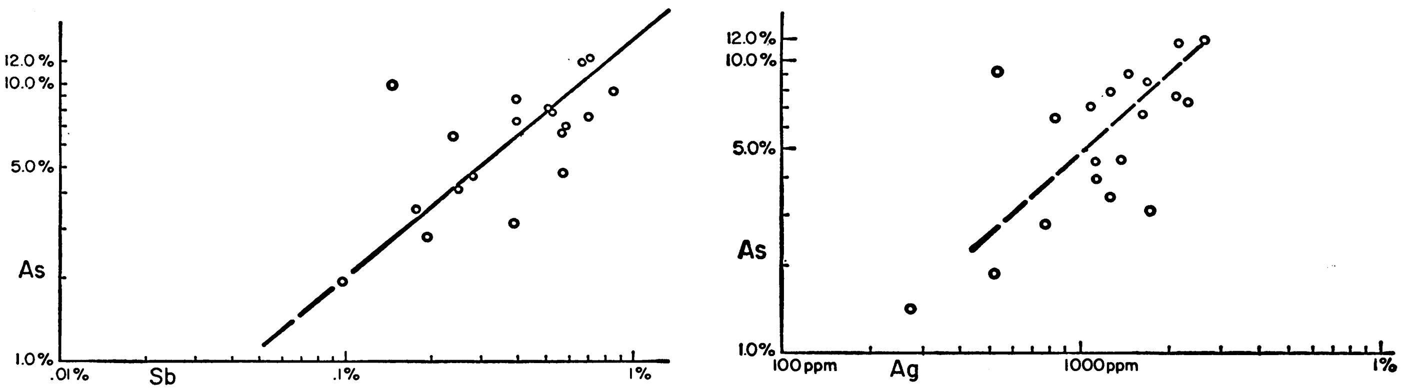

Fig. 3. Arsenic-antimony and arsenic-silver relations in the composition of copper ornaments.

The importance of this discovery lies in the fact that copper-arsenic alloy ornaments are very unusual. The trace-element content shows that copper sulf-arsenate ores must have been deliberately used for the easier manufacture of the ornaments. These ores were not in general use in the Middle East and even today no copper sulf-arsenate ore bodies are described in the geological literature other than those in Armenia (*5*). If the raw material for these ornaments did indeed come from Armenia, it must have traveled a supply route which existed in Chalcolithic times.

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DDT Antagonism to Dieldrin Storage in Adipose Tissue of Rats

Abstract. *Storage of dieldrin in the adipose tissue of female rats was markedly depressed when DDT and dieldrin were fed simultaneously. The amount of dieldrin present in the tissues of rats fed 1 and 10 parts of dieldrin per million was significantly reduced by the addition of 5 ppm DDT to the feed. The addition of 50 ppm DDT to the feed caused a 15-fold reduction in the amount of dieldrin stored in rats fed 1 ppm dieldrin, and a 6-fold reduction in rats fed 10 ppm dieldrin. This antagonistic effect of DDT suggests that the criteria used in predicting the pharmacological effects of combined residues of related insecticides need some revision.*

Members of the chlorinated hydrocarbon group of insecticides tend to accumulate in the tissue lipids of animals. When ingested orally or absorbed through the dermis, such compounds are retained for extended periods with only a slow rate of dissipation. Both DDT [1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane] and its metabolite DDE [1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethylene] are present in the tissue lipids of people in the general population of the United States (*1*). More recently, dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,-5,6,7,8,8a-octahydro-1,4-*endo,exo*-5,8-dimethanonaphthalene) and benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane) were found in the body fat of United States residents (*2*).

Some factors that affect the accumulation rates of such compounds in the body fat of animals have been studied, but with only one compound being tested at a time. This report concerns the amount of dieldrin stored in adipose tissue of rats after they were fed DDT and dieldrin simultaneously. Dieldrin storage was markedly depressed under the experimental conditions.

Seventy-two female rats weighing 100 g each were fed a basal diet of Purina laboratory chow (*3*). Recrystallized dieldrin was added at a concentration of 1 part per million or 10 ppm and recrystallized DDT at a concentration of 5 or 50 ppm. Cottonseed oil was incorporated into the diets at the rate of 1 percent to facilitate uniform dispersal of the insecticides. To the control diets, only 1 ppm or 10 ppm dieldrin was added. Each diet was fed to 12 rats. The rats were individually housed and fed for 10 weeks.

Methoxychlor [1,1,1-trichloro-2,2-bis-(*p*-methoxyphenyl)-ethane] was added to the diets of many individuals as a third variable. The methoxychlor did not affect the dieldrin storage pattern, however, and it is therefore not considered in this report.

All rats survived the feeding period. They appeared normal, and no significant differences in weight gains or food consumption were observed among them. A sample of adipose tissue was taken from the abdomen of each rat at the time of killing. This tissue was analyzed for lipid content and insecticide concentrations.

For anaylsis, 0.5 g of each tissue sample was ground in a mortar together with sodium sulfate, transferred to 100-ml centrifuge bottles and extracted five times with *n*-hexane. The five extracts were combined and concentrated to a 50-ml volume. A 1-percent portion was removed for the estimation of lipid by the dichromate oxidation procedure of Bragdon (*4*). The remaining extract was chromatographed on deactivated Florisil to separate the dieldrin present from the DDT and DDE (*5*). The dieldrin fraction was analyzed by gas chromatography with electron capture detection, a 5 percent Dow 11-Chromosorb W column operated at 180°C being used.

Table 1. Effect of DDT in the diet on the accumulation of dieldrin in adipose tissue of rats. Results are expressed as the mean values for groups of 12 rats ± standard error.

DDT added to diet (ppm)	Dieldrin found in tissue lipid (ppm)	
	1 ppm fed	10 ppm fed
0	15.1 ± 0.94	67.5 ± 2.7
5	5.4 ± 0.46	43.9 ± 2.4
50	1.0 ± 0.06	11.2 ± 0.62

The accuracy of the analytical procedure was checked by the following observations on representative samples. Duplicate analyses agreed closely. The standard deviation of the differences between duplicate samples was 0.5 percent of the mean dieldrin value (17.5 ppm) for a group of low dieldrin samples, and 7.4 percent of the mean dieldrin value (66 ppm) for a high dieldrin group. When dieldrin was added to tissue samples prior to analysis, recovery averaged 103 percent. When DDT was added prior to analysis of tissues containing dieldrin, no effect on dieldrin values was noted.

The concentrations of dieldrin found in the extractable lipids of the samples of adipose tissue are listed in Table 1 together with the various amounts of DDT administered.

Both concentrations of DDT in the diet markedly reduced the amount of dieldrin stored in the tissue. The incorporation of 50 ppm DDT in the diet caused a 15-fold reduction in the amount of dieldrin stored in rats fed 1 ppm dieldrin, and a 6-fold reduction in rats fed 10 ppm dieldrin. The DDT appeared to antagonize directly the storage of dieldrin. Both DDT and DDE accumulated additively in the adipose tissue according to the dosage of DDT. Data on this and other phases of the experiment will be published in detail elsewhere.

No research of this type has been reported previously, although pairs of chlorinated hydrocarbon insecticides have been tested for evidence of possible combined effects in insects. Storrs and Burchfield studied the nature of the joint action of several pairs of